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作品名稱 Plexiglas: from synthetic glass to cationic
exchanging resin

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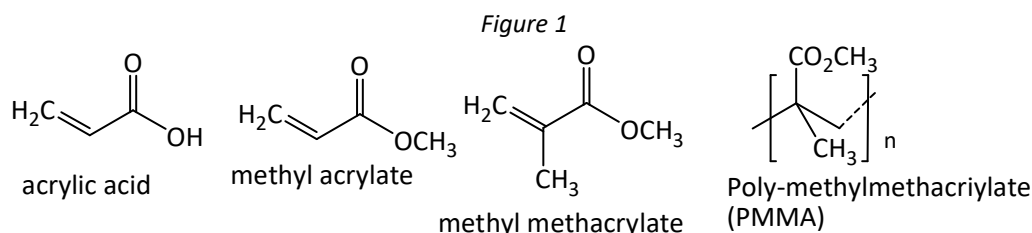
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INTRODUCTION

Plexiglas is a material used to replace glass. Plexiglas is a macromolecule made through the polymerization of the methyl-methacrylate^[1] to obtain polymethylmethacrylate (PMMA).



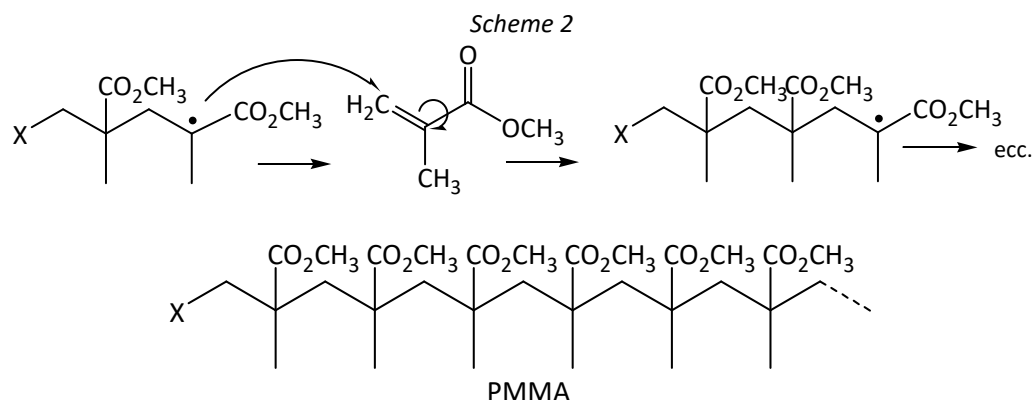
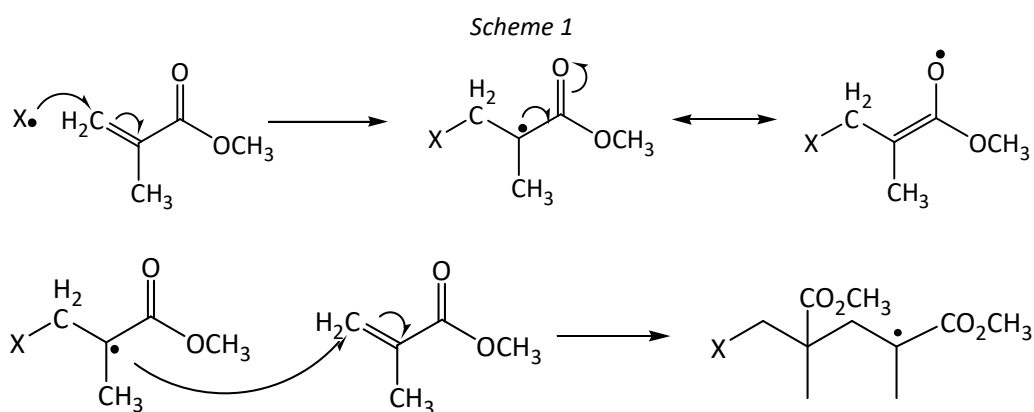
Note to the methyl methacrylate name: methyl refers to the methyl group ($-\text{CH}_3$) bound to the ester oxygen; the *meth* prefix of the methacrylate word, refers to the methyl group ($-\text{CH}_3$) bound to the carbon atom of the double bond.

OUTLINES OF POLYMERIZATION^[2]

Radical polymerization

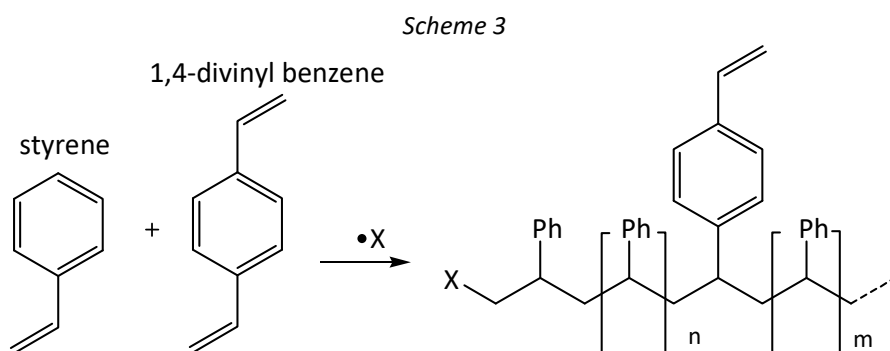
Conjugated alkenes with a carbonyl group ($\text{C}=\text{O}$), such as acrylates (compounds of the acrylic acid) are easily polymerized by means of different mechanisms.

So, it is often difficult to store these chemicals as they naturally polymerize when there are traces of weak nucleophiles (such as water) or radicals (also oxygen). Radical polymerization occurs very easily as the intermediate carbon radical is stabilized by resonance with carbonyl group. The X^\bullet radical starts the radical polymerization reaction.



It is known that it is possible to accomplish some reactions on polymers^[3]. The polyvinyl acetate can be transformed into polyvinyl alcohol through an alkaline hydrolysis; cellulose (polysaccharide of the plants wood) can be transformed into three-acetate of cellulose commonly defined “cellulose acetate”.

Another example concerns the *cross-linking reaction* of preformed polymers and the most important representative is the vulcanization of rubber. Preparation of the co-polymer between styrene and 1,4-divinylbenzene is also a cross-linking reaction.

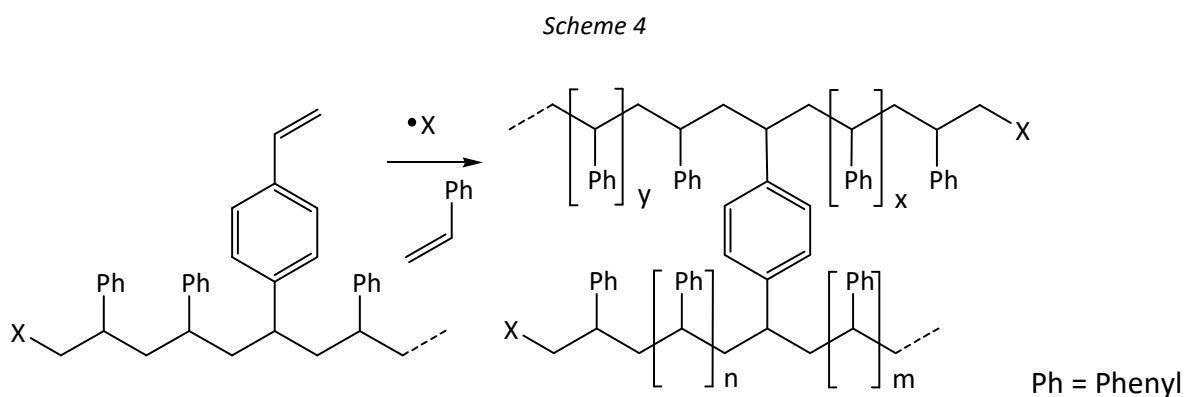


Ph = Phenyl

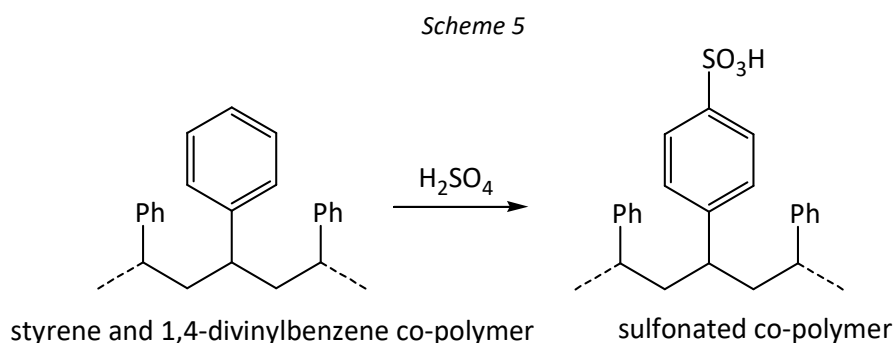
When a small amount of 1,4-divinylbenzene is co-polymerized with styrene, a linear polymer is obtained. In this polymer some phenyl rings have a 4-vinyl group. When another chain polymerizes close to it, the vinyl group of the former chain can be inserted in the new chain

of polystyrene; however only some free vinyl groups on the first chain will be included in the latter, during the polymerization reaction.

To achieve the required level of cross-linking, it is necessary to add enough 1,4-divinylbenzene.



A cation exchanging resin^[4] which has the $-\text{SO}_3\text{H}$ groups can be prepared starting from the co-polymerization of the styrene and 1,4-divinylbenzene. Polymerization is accomplished through an emulsion in water so that organic molecules are shaped like very small drops. The obtained polymer is shaped into very small pearls or similar form.



Ph= Phenyl

Along the frame of the polymer, there are some benzene rings. These can be sulfonated at the *para* position to insert the acid sulfonic group ($-\text{SO}_3\text{H}$)^[5]

A large amount of the benzene rings becomes sulfonated and the outer surface of every polymeric pearl is covered by the sulfonic group which is strongly acid. This polymer is an acid reactant and it is not soluble in normal solvents. It can be used to prepare a column or used as a heterogeneous reactant.

AIM OF THE RESEARCH

Preliminary remarks

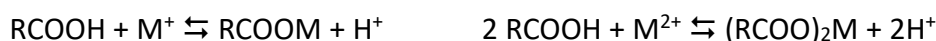
Evonik Plexiglas Industries^[6] manage a Plexiglas recycling plant in the Gramatneusiedl, a small Austrian town close to Vienna. In this plant, fused Plexiglas is warmed to 400 °C to separate its original components: methyl-methacrylate (MMA) and other substances. The solid substances are split from the gaseous MMA which is cooled to condense into liquid. This contains also other substances which were mixed with MMA before the Plexiglas preparation. These additives are eliminated through a distillation process which allows to obtain the MMA whose purity is 99%.

The aim of our research is to study an alternative recycling method which allows *to transform the polymer (Plexiglas) into a cationic exchanging resin*.

PRINCIPLE OF THE METHOD

Exchanging cationic resins^[7] have acid groups such as -COOH (*carboxylic; weak resin*) or $\text{-SO}_3\text{H}$ (*sulfonic; strong resin*). These resins fix cations solubilized in water releasing an equivalent number of protons:

Scheme 6

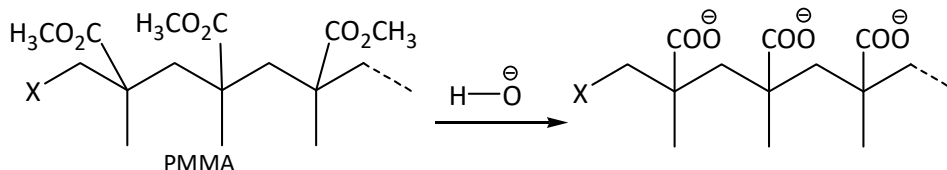


Regeneration is carried out treating the exhaust resin with an acid solution (diluted HCl) which moves both equilibria of the *scheme 6* to the left.

The basic idea of the Plexiglas recycling is the transformation of the ester group -COOCH_3 of the PMMA, into -COOH group by means of some reactions. First: *alkaline hydrolysis in order to change the -COOCH_3 group into carboxylate group, -COO^- (scheme 7)*. Second: *reaction with hydrochloride acid (HCl) in order to obtain the carboxylic group -COOH (scheme 9)*.

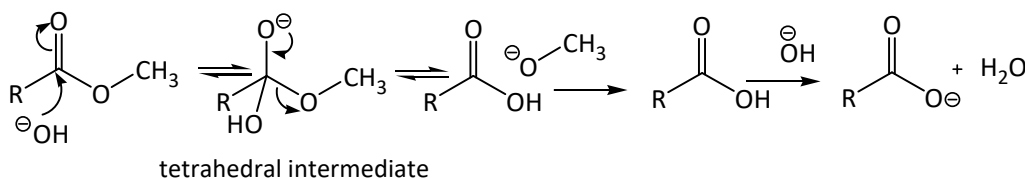
So, a polymer with properties of a cationic exchanging resin is obtained.

Scheme 7



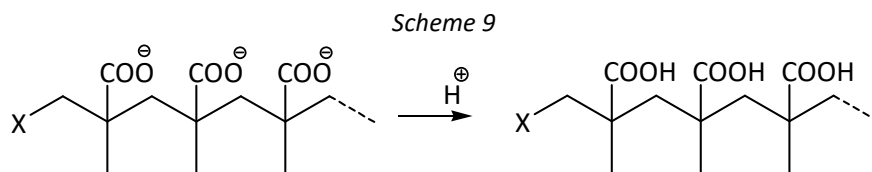
General mechanism of alkaline hydrolysis of esters^[8]

Scheme 8



The tetrahedral intermediate is named in this way because the central carbon atom changes its hybridization from sp^2 of the ester to sp^3 in the intermediate which has a tetrahedral geometry. In these types of reaction where the carbon atom of the carbonyl is attacked by a nucleophile, sometimes, the tetrahedral intermediate is stable enough to be isolated.

Acid treatment of Plexiglas after hydrolysis:



ESTERS REACTIVITY^[9]

Esters are a type of derivatives of carboxylic acids and they are little reactive compounds. The C–O group gives its *lone pair* of electrons, placed in the *p* orbital (*black lobes*) of the oxygen atom, to the anti-bonding orbital π^* (*red lobes*) of the C=O group (*figure 2*). Therefore, the ester stability increases and therefore they are less reactive.

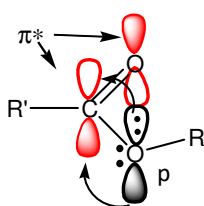


Figure 2

The donation of the lone pair of electrons proves the planarity of the ester group as only this geometry guarantees the parallelism between *p* and π^* orbitals; consequently, their interaction is possible.

{:}= *Lone pair* (unshared pair of electrons)

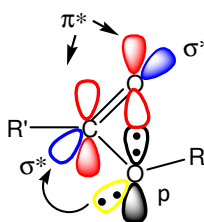


Figure 3a

Cis conformation (*more congenial*) of the R group and C=O group, in connection with the C–O single bond.

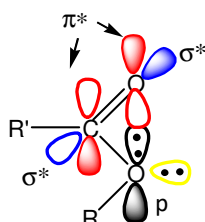


Figure 3b

Trans conformation of the R group and C=O group in connection with the C–O single bond. π^* and σ^* symbols show the empty anti-bonding orbitals

The *cis* conformation is more congenial because the other *lone pair* of electrons onto the oxygen atom (*single lob surrounded with a yellow line*) of the C–O group, can be shared with the σ^* anti-bonding orbital. Both orbitals have the suitable geometry and therefore the stabilization of ester increases. This sharing is not possible in the *trans* conformation as both the orbital which holds the lone pair of electrons onto the oxygen atom and the σ^* orbital do not have the suitable geometry to share electrons.

EXPERIMENTAL PART

Equipment

- Drill with adjustable speed and a cobalt-steel twist drill ($\phi=5.5$ mm)
- Electric heater equipped with magnetic stirrer. Small scissors and scalpel made of stainless steel.
- Filter paper. Glass wool
- Stainless steel filter for infusion shaped as a hemispheric form ($\phi_{\text{HOLES}}=0,85$ and 1mm)
- *Thermometer* (sensibility 0,1°C)
- *IR spectrophotometer* working with Fourier transform. It is equipped with universal ATR (Attenuated Total Reflectance) system with diamond contact point and one bounce. It has a beam splitter made of CsI. The detector for the middle infrared is made of DTGS (Three-Glycine Sulphate). Wave-number range = 4000–650 cm^{-1} with a resolution of 0,5 cm^{-1} . This equipment can exclude the signal distortion caused by steam and CO_2 .
- *Visible and UV (double beam) spectrophotometer* equipped with a halogen lamp for the visible range and a deuterium lamp for the UV range. Wave length range=190–1100 nm. Wave length accuracy= $\pm 0,1$ nm. Band width=1 nm. Automatic lamp change at 326 nm.

Reactants

- Transparent and colourless Plexiglas slabs (thickness 3 and 6 mm)^[10].
- Anhydrous ethanol (CH₃CH₂OH).
- Solid KOH (purity 85%).
- Solid NaOH (purity 97%).
- Hydrochloride acid (concentration=37% m/m)

SYMBOLS AND INSTRUMENTAL PARAMETERS^[11]

| | |
|---|--|
| t (°C), (temperature measured in Celsius degrees) | <i>experimental uncertainty</i> for the average value of a set of measures: $\langle x \rangle \pm \sigma_x$ |
| t (h), warming time measured in hours | \curvearrowright , curved arrows to show the electrons movement |
| $\bar{\nu}$, wave number measured in cm ⁻¹ | \sum , summation symbol |
| $\langle \rangle$, average value of a physic property | T, transmittance |
| $\langle X \rangle = \frac{x_1 + x_2 + \dots + x_n}{n}$ | T%, percentage transmittance |
| $\sigma_x = \sqrt{\frac{\sum (x - \langle x \rangle)^2}{n-1}}$ = Standard Deviation | A, absorbance; $A = -\log T$ |
| for a set of measures. It is approximated to the first significant figure and used as the | D, derivative |
| | pH, [H ⁺] concentration |
| | \rightarrow , reaction symbol |
| | \rightleftharpoons , equilibrium reaction symbol |

GENERAL METHOD

A Plexiglas sample is prepared drilling the Plexiglas slabs (*photo 1*) to obtain some grams of shavings^[12] (*photo 2*). Their dimension is reduced by means of a mixer for food to obtain granules (*photo 3*) which can go through the holes of the steel filter for infusion. A portion of the sample is used to record IR spectra and some of its grams are subjected to the alkaline hydrolysis reaction. Among granules of the Plexiglas sample there are some small dark fragments. These are attracted by a magnet. They are ferrous particles arising from the mixer blade which wears out during its whirl to bang the hard shavings of Plexiglas. The ferrous particles are separated from Plexiglas granules through a magnet. Some ferrous particles are solubilized by means of concentrated HCl. The following reaction $\text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2$ occurs. The solution with the iron ion (Fe^{2+}) is exposed to air oxygen to oxidize it to Fe^{3+} according to the reaction $4\text{Fe}^{2+} + 4\text{H}^+ + \text{O}_2 \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}$. A portion of this solution is used to carry out the distinctive test for ferric ion (Fe^{3+}) through the reaction with potassium thiocyanate (KSCN)^[13].

The test is positive due to the reaction: $\text{Fe}^{3+} + \text{SCN}^- \rightleftharpoons [\text{Fe SCN}]^{2+}$

The dark red ion $[\text{Fe SCN}]^{2+}$ [iron (III) thiocyanate] is formed: it is the mark that the ion (Fe^{3+}) is present. 0,5 mL of ethylic ether are added to this solution; the ethereal layer is stratified above water and it changes to a red colour after shaking the mixture. On the contrary water becomes almost colourless. It means that ether has taken away the iron (III) thiocyanate complex.

In a preliminary experiment, hydrolysis of Plexiglas is carried out through an aqueous solution of NaOH (10% m/V). 0,52 g of the Plexiglas granules and 30 mL of the NaOH aqueous solution are mixed and the mixture is warmed to the reflux temperature and the reaction lasts 6 hours. At the end, the solid component is separated, and it is rinsed with de-ionized water until the pH of water after rinsing, is about 7. The solid is naturally dried, then it is used to record IR spectra: there are not remarkable differences between IR spectra of the original Plexiglas and IR spectra of the solid after hydrolysis. It means that no reaction is occurred; it means that water is not the suitable solvent. Anhydrous ethanol (CH₃CH₂OH) is chosen as a solvent because its molecule has bigger affinity

to Plexiglas than water and it can better transport KOH or NaOH inside granules. In this research methanol (CH₃OH) could be used but it has not been chosen because it is very toxic, even though it would be a better solvent. Its molecule is smaller than ethanol molecule therefore it penetrates better inside the granule; then it is a more suitable solvent. Hydrolysis is carried out by means of KOH or NaOH (10% m/V) in anhydrous ethanol. The mixture is put in a single-neck flat bottom flask (250 mL) equipped with a bulb condenser. In the experiments the mixture is warmed to the reflux temperature through a sand bath and electric heater. The mixture is stirred by means of a magnetic stirrer. The reflux temperature is about 82–84 °C and it is different according to the type of the pre-arranged experiment. When the hydrolysis is completed, the solid is separated through settling from the solution whose colour is dark brown. The solid is rinsed many times with alkalinized ethanol (7 < pH < 8; universal indicator paper). To obtain the rinsing solution it is necessary to add some drops of the hydroxide solution to some volume of anhydrous ethanol. The rinsing operation ends when the solution is nearly colourless. Then some rinsing with anhydrous ethanol is performed. The solid is naturally dried and a portion of this is used to record IR spectra. The size of the remaining solid is reduced through scissors and scalpel; it is put in a small beaker with some diluted (1:2) HCl for some days. After this acid treatment, solid is separated through settling and filtration. This solid is rinsed with de-ionized water (6 < pH < 7; universal indicator paper) until the chloride ions (Cl⁻) disappear. The test with AgNO₃; Ag⁺ + Cl⁻ → AgCl (solid)^[14] is carried out. The solid is naturally dried. This solid is used to record IR spectra and to prepare micro-columns which are used to percolate some mineral water to verify the capability of resin to capture metallic cations.

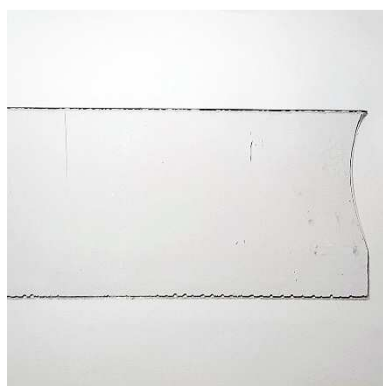


photo 1
Original Plexiglass



photo 2
Plexiglass Shavings



photo 3
Granular Plexiglass

IR SPECTRA RECORDING

IR spectra are recorded putting one or more small pieces of solid material on the top of the diamond crystal of the ATR platform of the IR spectrophotometer. Fragments are pressed against the crystal through the mechanic arm. A convenient number (from 7 to 10) of spectra is recorded for every sample. The quality of these spectra is always “passed”; if it is not, spectra are repeated. As the number of experimental spectroscopic data to process is very large, the *average spectrum* of the spectra set of every sample is calculated. This average spectrum is used to study the absorption characteristic bands of the sample. The average spectrum is calculated by the instrument’s software.

IR SPECTRA ANALYSIS^[15]

IR spectra analysis is carried out referring to the standard values of the absorption bands which are shown in brackets in *table 1*. These data are taken from the mentioned bibliography.

Figure 4 IR spectrum of the **Poly-Methyl-Methacrylate** (PO0069 PMMA)^[16]

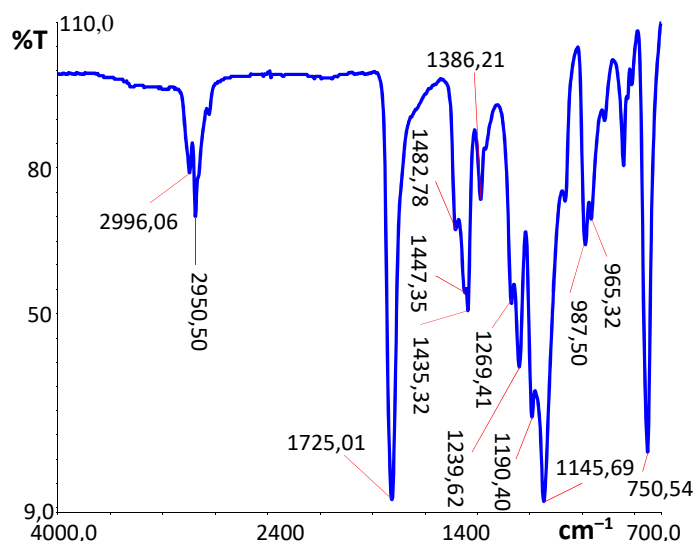


Table 1

| $\bar{\nu}$ (cm^{-1}) | Assignment |
|----------------------------------|--|
| ≈ 2996 (2992) | O-CH ₃ , C-H stretching |
| ≈ 2950 (2948) | C-CH ₃ , C-H stretching |
| ≈ 1725 (1729) | C=O stretching |
| ≈ 1483 (1485) | CH ₂ bending (scissoring) |
| ≈ 1447 (1450) | O-CH ₃ (CH ₃ a-sym. bending) |
| ≈ 1435 (1434) | O-CH ₃ (CH ₃ sym. bending) |
| ≈ 1386 (1382) | C-CH ₃ (CH ₃ a-sym. bending) |
| ≈ 1269 (1265) | O=C-O-C; O-C stretching |
| ≈ 1240 (1238) | O=C-O-C; C-O stretching |
| ≈ 1190 (1189), | C-O-C bending |
| ≈ 1146 (1145) | CH ₂ bending (wagging e/o twisting) |
| ≈ 965 (962) | C-CH ₃ a-sym. bending |

Figure 5 IR average spectrum of the ten spectra of the commercial Plexiglas

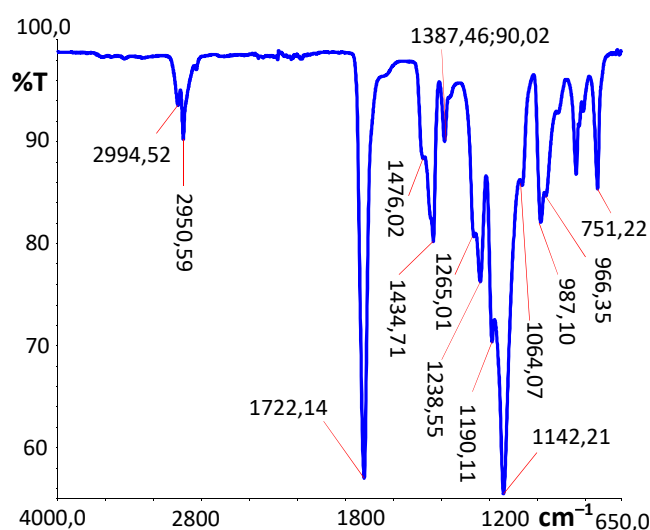


Table 2

| $\bar{\nu}$ (cm^{-1}) | Assignment |
|----------------------------------|---|
| ≈ 2995 (2992) | O-CH ₃ , C-H stretching |
| ≈ 2951 (2948) | C-CH ₃ , C-H stretching |
| ≈ 1722 (1729) | C=O stretching |
| ≈ 1476 (1485) | CH ₂ bending (scissoring) |
| ≈ 1435 (1434) | O-CH ₃ bending (CH ₃) |
| ≈ 1387 (1382) | C-CH ₃ bending (CH ₃) |
| ≈ 1265 (1265) | O=C-O-C; O-C stretching |
| ≈ 1239 (1238) | O=C-O-C; C-O stretching |
| ≈ 1190 (1189) | C-O-C bending |
| ≈ 1142 (1145) | CH ₂ bending (wagging e/o twisting) |
| ≈ 966 (962) | C-CH ₃ sym. bending (CH ₃) |

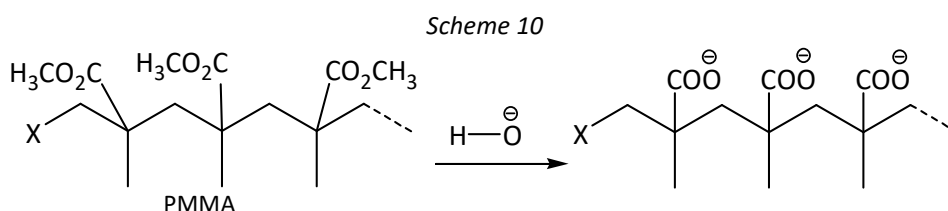
In the tables close to spectra both the main infrared bands of the PMMA (*instrument library*) and those of the commercial Plexiglas, are shown. If some vibrations have two bands their assignation is shown twice inside the corresponding box. The comparison between PMMA spectrum of the library and the commercial Plexiglas spectrum gives a compatibility of the 95,5%. It is not 100% as the commercial Plexiglas contains other substances in addition to the PMMA.

FIRST EXPERIMENT

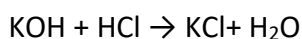
Procedure

In this first experiment, KOH is used as it quickly solubilizes in anhydrous ethanol unlike NaOH^[17]. 50mL of a KOH solution in anhydrous ethanol are prepared (concentration = 8,5 % m/V). An

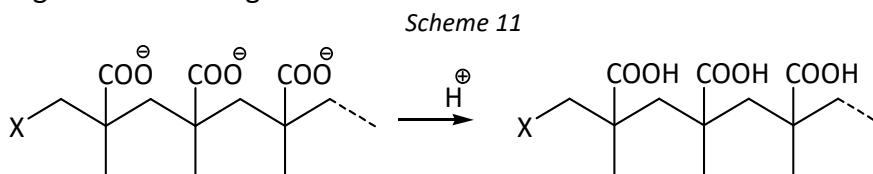
amount of 0,5 g of small granules of Plexiglas, is put in a single-neck flat-bottom flask (250 mL) to react with 35 mL of the KOH alcoholic solution. The mixture is warmed to the reflux temperature through a sand bath and an electric heater, stirring the mixture by means of a magnetic stirrer. The reflux lasts six hours. After the beginning of the boiling, the granules agglomerate becoming a spongy and milky solid. A doubt arises: this phenomenon could be a consequence of the solvent effect. To solve the question, a second reaction is carried out using 0,2 g of Plexiglas and 30 mL of anhydrous ethanol which are warmed to reflux temperature for five hours. After the beginning of boiling the same phenomenon as the first reaction is observed. Some tests to explain this phenomenon are accomplished. A small amount of the suspension of the first reaction (1÷2 mL at the end of the reflux) is put in a test tube and de-ionized water is added to obtain a double volume. The solid in suspension disappears and the solution becomes clear (also the day after the solution looks clear); the solution pH is ≈ 12 (universal indicator paper). A possible explanation is based on the alkaline hydrolysis of Plexiglas according to the following reaction:



The carboxylate ions ($R-COO^-$) are polar groups; they “solubilize” in water (polar molecule) as they have affinity for this; they are *hydrophile* groups. The alkyl chain is not polar, it is a hydrophobic group therefore it has affinity for ethanol (little polar) and, then, solubilizes in this. As water and ethanol are miscible according to any proportion, the resultant macromolecule becomes soluble in the ethanol–water mixture. This assumes that the small amount of Plexiglas is hydrolysed completely. A portion of this solution is put in a test tube and is made acid by the concentrated HCl till $pH \approx 0,5$. A solid like a gel is made in suspension; it is visible also the day after. It could merely be KCl which is produced by the reaction:



However, KCl is soluble in water and slowly soluble in ethanol. So, it seems little believable unless a large amount of KCl is produced so that the solution is saturated. Another possible explanation concerns the carboxylate ions ($RCOO^-$) which can be changed into carboxylic group ($RCOOH$) by the acid, according to the following reaction:



The resulting polymer has $R-COOH$ groups much less polar in comparison with the corresponding anion, then it could not be soluble into water/alcohol/HCl (aq) mixture. Both phenomena could occur. A small amount of the suspension which is obtained after reflux boiling of the Plexiglas–anhydrous ethanol mixture (without KOH) is put into a test tube and some de-ionized water is added to obtain a double volume. The suspension persists without changing also the day after. The suspension pH is $\approx 6,4$ (universal indicator paper). Other examinations were not carried out about two suspensions after reflux boiling. In conclusion there are signs that alkaline hydrolysis occurs when Plexiglas is put to react with KOH in ethanol at the reflux temperature. A rinsing solution for the solid obtained after reflux is prepared using anhydrous ethanol alkalized from its $pH \approx 5,5$ to $7 < pH < 8$ (universal indicator paper) by means of the ethanolic solution of KOH.

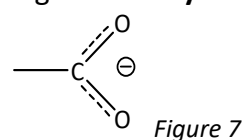
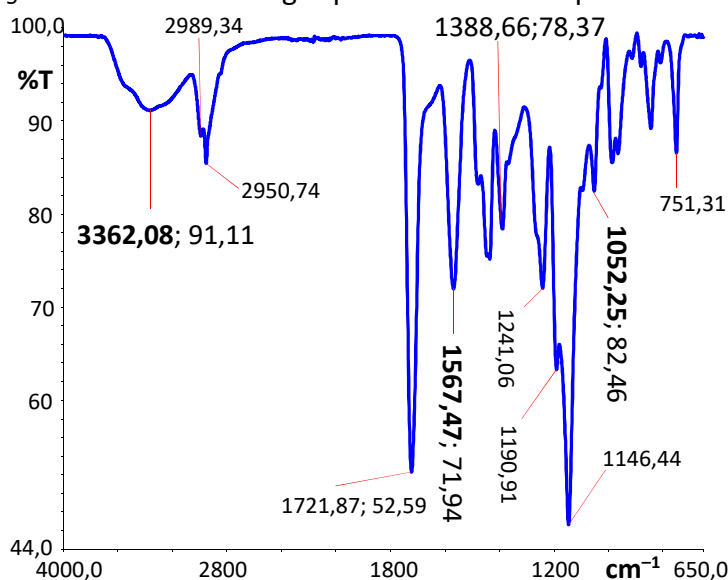
The KOH solution, before being used, is filtered through a filter paper (quantitative, slow) because it contains a light opalescence which may be potassium carbonate not soluble in ethanol. It is

formed due to the reaction between KOH and CO₂ of the air. Opalescence could be also due to other impurities, not soluble in ethanol. The solid which is obtained after hydrolysis, is split from the solution by settling: it is a spongy and milky-white solid. The ethanol solution is pale yellow; it could be the result of the reaction: $\text{CH}_3\text{CH}_2\text{OH} + \text{KOH} \rightarrow \text{CH}_3\text{CH}_2\text{OK} + \text{H}_2\text{O}$, where potassium ethoxide (CH₃CH₂OK) is formed; its colour is yellow. This colour becomes dark during the following days. This reaction is possible as the KOH concentration is very great. A small amount of the solid obtained after the Plexiglas hydrolysis is split by settling and it is inserted in a 50 mL beaker and it is rinsed many times by means of the rinsing solution. Then it is rinsed with anhydrous ethanol and at the end with the rinsing solution, so that the pH of the liquid has a value close to seven. The solid is gummy and sticky; it is not white-milky, but it is clear and colourless. It is naturally dried and at the end it turns into hard material. A small amount of the dried solid is used to record IR spectra (*figure 6*). Another amount of the solid is introduced into an Erlenmeyer flask (25 mL) and 2÷3 mL of the concentrated HCl is added to it for six days at room temperature. The flask is closed with its frost-ed-glass stopper and parafilm. After the addition of the concentrated HCl, the solution is yellowish due to the likely presence of the Fe³⁺ ions. These can arise from the small metallic pieces released by the blades of the mixer used to cut up Plexiglas and not completely removed. At the end of the acid treatment period, the yellowish solution is now almost colourless, and the pH is basically zero. A portion of this solution is used to perform the test for the Fe³⁺ ions, previously mentioned: it is positive. The solid is rinsed with de-ionized water till chloride ion (Cl⁻) disappears (test with AgNO₃, previously described). The hypotheses that support the change of Plexiglas into cationic exchanging resin, are validated by infrared spectroscopic examinations, shown in the next spectra explanation.

FIRST EXPERIMENT RESULTS

Since this first experiment is preparatory for the research, only three spectra of the solid obtained after Plexiglas hydrolysis, are recorded. The average spectrum of them is shown in *figure 6*. The comparison between the original Plexiglas spectrum (*figure 5*) and the spectrum of the solid after hydrolysis (*figure 6*) shows, in this latter, three new bands. The band at ≈ 1567 is narrow and strong; the band at ≈ 1052 is narrow and medium; the band at ≈ 3362 is broad and medium. The value of some bands in the spectrum, is kept as a reference to compare to the original Plexiglas spectrum.

Figure 6 IR average spectrum of three spectra of the Plexiglas **after hydrolysis** with KOH



The band at ≈ 1567 is the asymmetric stretching (1610-1550) of the carboxylate anion which is depicted in *figure 7*. The symmetric stretching (1420-1300) is more difficult to detect because it lies in that spectrum area where there are other absorption bands belonging to the original Plexiglas. (*figure 5*).

However, it can be hypothesized that the mentioned band is that at 1388,66 ($T\%=78,37$; $A=0,1058$) already existent in the original Plexiglas spectrum at 1387,46 ($T\%=90,02$; $A=0,0457$). It is due to the C-CH₃ bending (*figure 5*). The increase of the intensity of this band in the spectrum of the solid after hydrolysis (the absorbance changes from the original value, 0,0457 to 0,1058) shows that it is due to the new carboxylate ion, RCOO⁻ produced by the reaction depicted in the *scheme 7 or 10*. The transmittance of the same band at 1387,61 of the spectrum of the hydrolysed Plexiglas and treated with HCl (*figure 8*) is $T\%=87,40$ ($A=0,0585$). The absorbance is much smaller than the absorbance of the same band (1388,66) after just the hydrolysis in the spectrum of *figure 6* ($T\%=78,37$; $A=0,1058$). Moreover $T\%$ and A values of the spectrum of the *figure 8* are close to the values of the same band at 1387,46 ($T\%=90,02$ and $A=0,0457$) of the original Plexiglas spectrum (*figure 5*). This result shows that the band at 1388,66 of the spectrum of the *figure 6*, belongs both to the C-CH₃ bending of the original Plexiglas (*figure 5*) and to the symmetric stretching of the carboxylate ion (*figure 7*).

The carboxylate ion disappears after the acid treatment so a diminution of the absorbance of its stretching band should happen. This phenomenon really occurs (spectrum *figure 8*).

The band at 3362,08 could be the O-H stretching of ethanol (3400-3200) absorbed by polymer and held after rinsing and drying the solid. To support this hypothesis there is the band at 1052,25 (stretching C-O, ≈ 1050 , primary alcohol). However, there is another explanation: it is possible that the tetrahedral intermediate (*scheme 8*) is so stable to be found in the solid obtained after hydrolysis. Stability can be the result of the formation of many hydrogen bonds due to the huge number of O-H groups. As it is an alcohol the IR absorption bands already mentioned about the *figure 6*, will be present. Spectral analysis emphasized that the partial hydrolysis of Plexiglas has occurred; consequently, the ester C=O band at 1721,87 is still very strong (*figure 6*).

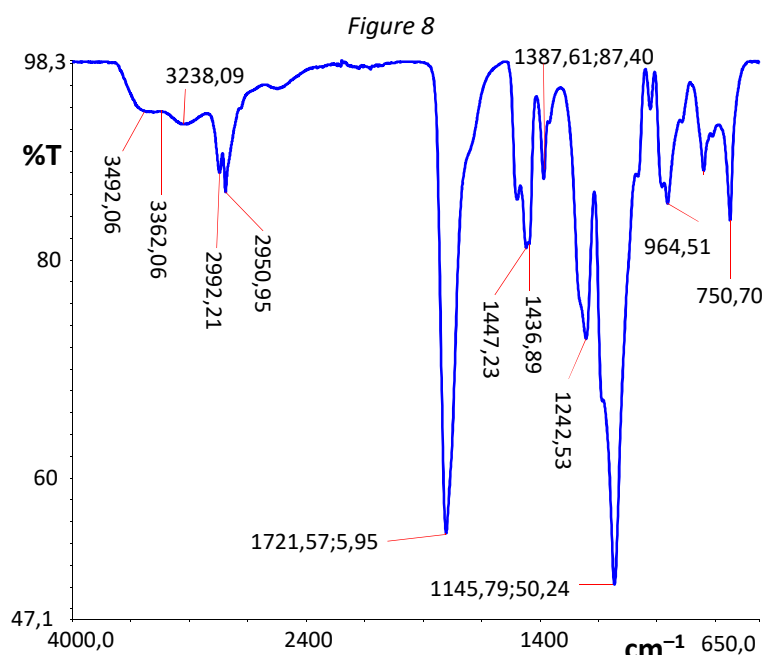
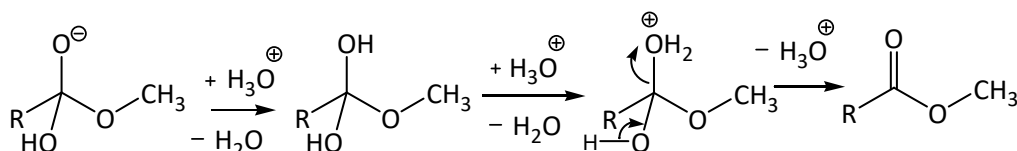


Figure 8 shows the average spectrum of the seven spectra of the solid that arises from Plexiglas hydrolysis with KOH and after the treatment with HCl. The comparison with the spectrum of the hydrolysed Plexiglas (*figure 6*) shows the disappearance of the band at 1567,47 of the COO⁻ ion. Also, the band at 3362 has disappeared. In its place, a hollow and two bands (3238,09 and 3492,06) at its sides, come out. The first band is the O-H stretching of the carboxylic acid (3300-2500); the second can be the O-H stretching of water (3490) (solid can have trapped

some moisture after the rinsing with de-ionized water). The band at 1721,57 is the C=O stretching of the acid (1725-1700) which overlaps to the band of the same group at 1722,14 of the original Plexiglas (*figure 5*). The analysis of the spectrum in *figure 8*, shows the band of the carboxylic group (-COOH) after the hydrolysed Plexiglas has been treated with HCl. The acid treatment causes the tetrahedral intermediate collapse to ester according to the reactions of the *scheme 12*. This process explains the "disappearance" of the band at 3362,08.

Scheme 12



Tetrahedral intermediate

The tetrahedral intermediate, with an acid (HCl), changes to ester and, then, the alcoholic group (OH) disappears and consequently also the IR corresponding band disappears. This reaction, together with other reasons, would explain why the hydrolysis reaction does not progress till the total change of Plexiglas. In the second experiment the same limitation occurs, despite the hydrolysis reaction goes on for 65 hours.

SECOND EXPERIMENT

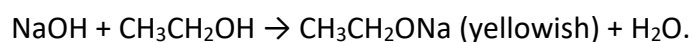
Procedure

To do this experiment, 100 mL of a solution of NaOH in anhydrous ethanol (10% m/V) are prepared.

Calculus of the required amount of NaOH 97% (m/m); $97\text{g} : 100 = 10\text{g} : x$; $x = 10,31\text{ g}$

The weighted mass of NaOH is put in an Erlenmeyer flask (100 mL) together with 70-75 mL of solvent and stirred through a magnetic stirrer to make the solubilization of the solute easier.

NaOH solubilization is very slow and the process requires about 24 hours. The solution is straw-yellow, due to the presumable formation of sodium ethoxide according to the reaction:



This reaction is possible owing to the high concentration of NaOH. The solution is poured into a 100 mL flask and its volume is increased to the mark with solvent. An amount of 10g of granules Plexiglas, prepared in the mentioned way, is separated from the ferrous residue by means of a magnet (ferrous residue comes from the wear of the mixer blade). It is put in a single-neck flat-bottom flask (capacity, 250 mL) with a bulb condenser on the top, together with 100mL of ethanolic solution of NaOH. The mixture is warmed to reflux temperature through a sand bath and an electric heater. The reflux temperature is 84 °C and the reflux is carried out in a discontinuous way for practical requirement. The overall first reflux period lasts about 22 hours at the end of which the solution is a dark brown colour. This is separated and removed by the solid settling and it is substituted with 100 mL of a fresh ethanolic solution of NaOH. Before introducing this fresh solution in the flask, solid is rinsed with anhydrous ethanol. This second reflux continues for a period of 25 hours at the end of which a second substitution of the exhaust solution is accomplished with 80 mL of a fresh ethanolic solution of NaOH. The reflux resumes till getting a total period of 65 hours for the three periods of treatment. At the end of this whole period, the exhaust solution is split by settling and the solid is rinsed by ethanol whose pH is adjusted between 7 and 8 (universal indicator paper) by means of the addition of some drops of ethanolic solution of NaOH. Rinsing is carried on with ethanol till the rinsing solution is almost colourless and its pH is slightly acid. In every rinsing the solution is split from the solid by settling. Solid is put in a small crystallization vessel and it is naturally dried. After drying the solid looks as shavings which have a faint yellow-ochre colour (*photo 4*); its mass is 12g. It has increased by 2g in comparison with the starting mass of Plexiglas (10g). The mass increase is caused by the partial substitution of the ester group ($-\text{COOCH}_3$; formula mass=59) with the carboxylate ($-\text{COO}^- \text{Na}^+$; formula mass=67). A small amount of the dried solid is used to record IR spectra. The remaining mass (11,5g) is put in a 250 mL beaker and treated with 100 mL of diluted (1:2) HCl prepared with a concentrated solution of HCl. The mixture is kept till the following day when the solution is dis-

charged and substituted with 100 mL of a fresh solution of diluted acid. The solid and the solution are kept in contact for 4 days, at the end of this period, the solid is split from the solution by settling and then is rinsed with de-ionized water ($6 < \text{pH} < 7$; universal indicator paper). Rinsing goes on till the whole disappearance of the chloride ion (Cl^-); (test with AgNO_3 already mentioned).

The solid is then put in a watch glass to dry naturally; after drying the solid is yellow-ochre and its mass is 8,4 g (*photo 5*). The comparison with the starting mass (11,5) shows a decreasing of 3,1g. This is caused by the substitution of the carboxylate group ($-\text{COO}^- \text{Na}^+$; formula mass=67) with the carboxylic group ($-\text{COOH}$; formula mass=45). A small amount of the solid is used to record IR spectra; the remaining solid is used to prepare *micro-columns* to elute some mineral water and to measure its "hardness" before and after percolation through the micro-columns.



photo 4
hydrolysed Plexiglas



photo 5
hydrolysed Plexiglas and treated with HCl

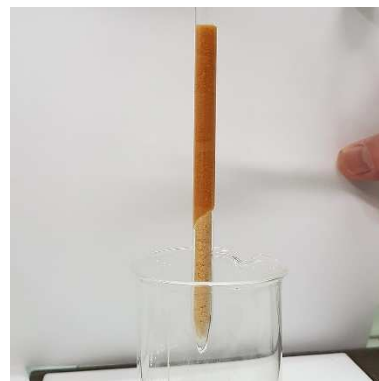


photo 6
micro-column

To make micro-columns a glass tube (inside diameter = 6mm; length ≈ 20 cm) is used. One end of the tube is shaped with a Bunsen flame to have a very small opening (about 1 mm; micro-column bottom). A small flock of glass wool is inserted inside the column at the bottom, close to the exit (small opening); it works as a stopper. An amount of 1,5 g of hydrolysed Plexiglas and treated with HCl, is introduced inside the column to make a steady phase, whose height is about 80 mm (*photo 6*). The size of the solid material has been graded by means of the metallic sieve for infusion before introducing it inside the column. When 1,316 g of the solid is sieved, an amount of 1,202 g of solid go through the holes of sieve and $1,316 - 1,202 = 0,114$ g, that is 8,7% of the whole do not go through the sieve. *Photo 6* shows that the micro-column seems to split in two parts which have different diameters. Actually, it is an optical effect because the upper dark zone is already wet with water; on the contrary the lower pale zone is still dry as water has not got to it. Mineral water is percolated through every column prepared in that way: the colour of the first volume of water that comes out of the column is yellowish.

Table 3

| Investigation |
|--|
| hardness measure |
| pH measure |
| Spectrophotometer measure in the Visible range |

The investigations shown in *table 3* are carried out both on the percolated water and the original water.

Remark to the rinsing of the solid obtained from Plexiglas hydrolysis.

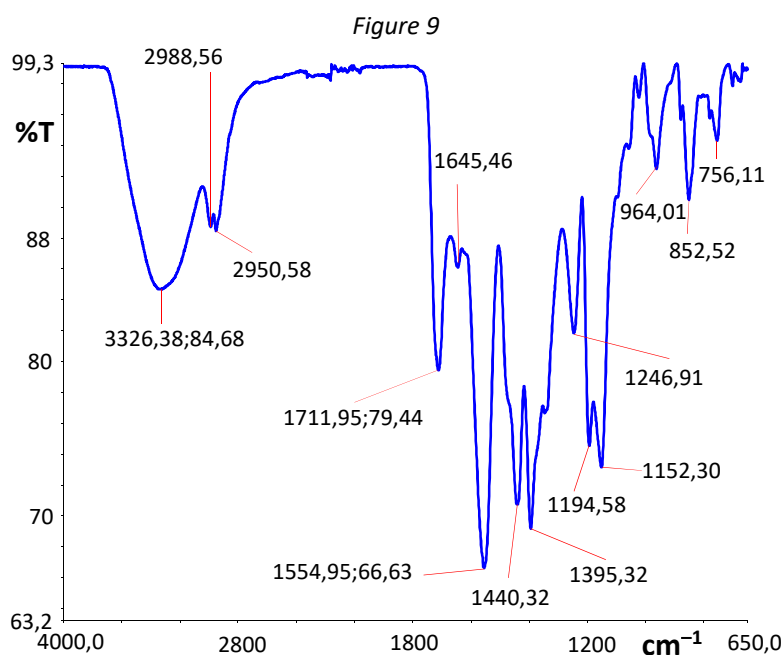
In an experiment the solid is rinsed with a solution slightly alkaline ($\text{pH} \approx 8$) of a mixture with the same ratio of ethanol and water.

Steps: 1-*adding* of the solvent mixture to the solid: a gel is obtained, 2-*flocculation* with solid NaCl, 3-*separation* and *drying* of the flocculated solid, 4-*mechanic separation* of the solid NaCl, 5-*separation* with little water of the residual solid NaCl, 6-*filtration under vacuum* and *drying* of the thick gel. During these steps a large amount of solid is lost, so this very complicated and little profitable rinsing method is not suitable.

SECOND EXPERIMENT RESULTS

Figure 9, shows the “average spectrum” of ten spectra of the solid obtained after Plexiglas hydrolysis for 65 hours. **Spectrum analysis:**

A very strong band at 1554,95 corresponding to the asymmetric stretching of the carboxylate group (COO^- : 1610-1550) comes out. The symmetric stretching (1420-1300) of the same group is very difficult to find out as it should be in a spectrum range where there are already many absorption bands of the original Plexiglas (figure 5). There is, also, a strong and wide band at 3326,38 which corresponds to the O–H group stretching. It could belong to the tetrahedral intermediate, to the residual ethanol absorbed by particles of hydrolysed solid or to the water absorbed as moisture during the drying of solid. Moreover, it could belong to all the components or to two components of the list. The hypothesis of the water presence is supported by the medium intensity band at 1645,46 of the water bending (H–O–H ; 1645).



There is also the band of ester C=O stretching of the original Plexiglas at 1711,95 (see figure 5). The lengthened hydrolysis of this experiment has caused a clear and massive transformation of the original Plexiglas. The reaction changes the group ester, COOCH_3 into the sodium salt of the carboxylic acid (scheme 7)

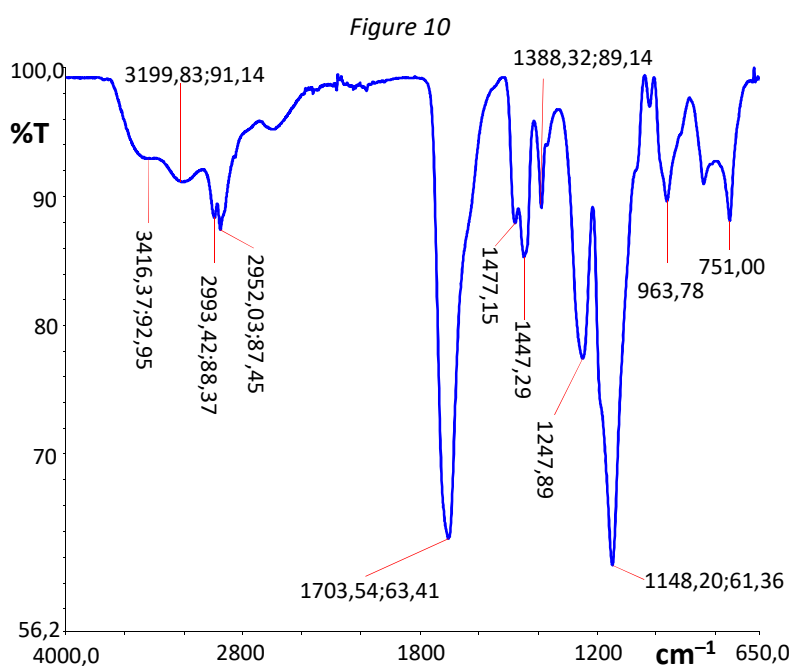
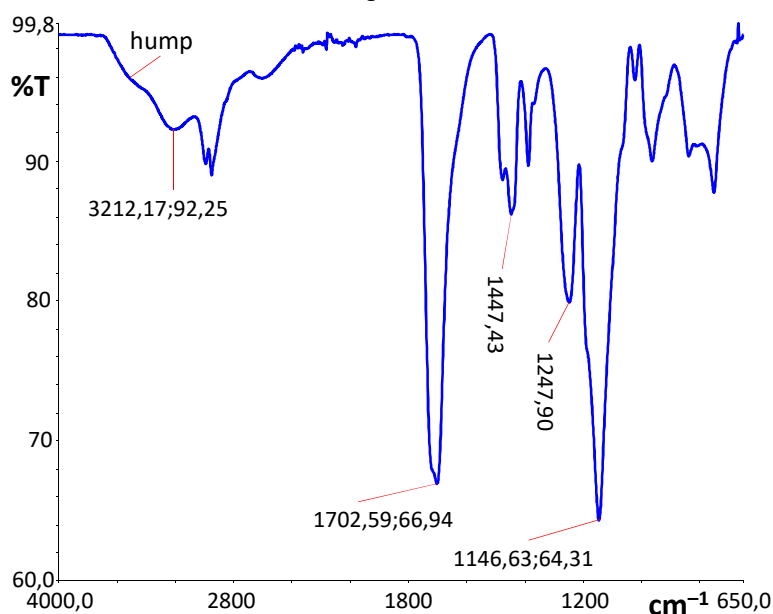


Figure 10 shows the average spectrum of ten spectra of the hydrolysed Plexiglas and treated with dilute (1:2) HCl. This spectrum, in comparison with the spectrum of figure 9, shows the disappearance of the bands at 1554,95 and at 3326,38. In place of this latter, two bands appear at 3416,37 and at 3199,83. The latter is O–H stretching of the carboxylic group (COOH) of the acid (3300–2500). There is a strong band at 1703,54 of the C=O stretching. To find out the band at 3416,37 can belong to, a small amount of the solid is put into a stove at 105°C for 6 hours.

Seven spectra of the “dried” solid are quickly recorded; their average spectrum is shown in figure 11.

Figure 11



The comparison between the spectrum of *figure 11* and the spectrum of *figure 10*, allows us to find out that the band at 3416,37, of the spectrum of *figure 10*, has changed into a hump which arises on the left side of the spectrum of *figure 11*. This means that the original band at 3416,37 belongs to the O–H stretching of the water. The warming at 105 °C has reduced the moisture of the solid, then the band intensity has decreased. There is another element that accounts for the phenomenon.

The band at 3212,17 belongs to the O–H stretching of the COOH group and its wave-number is slightly higher than the value (3199,83) of the spectrum of *figure 10*. The content of the moisture has decreased, then there are less hydrogen bonds between the water molecules and the carboxylic groups (COOH). These become freer in comparison with the same groups of the not dried solid. Therefore, the wave-number increases. Considering the band of the C=O stretching at 1702,59 (*figure 11*), it is possible to find out that it consists of two overlapped bands. To split them the fourth derivative with 37 points of the band is calculated.

Figure 12

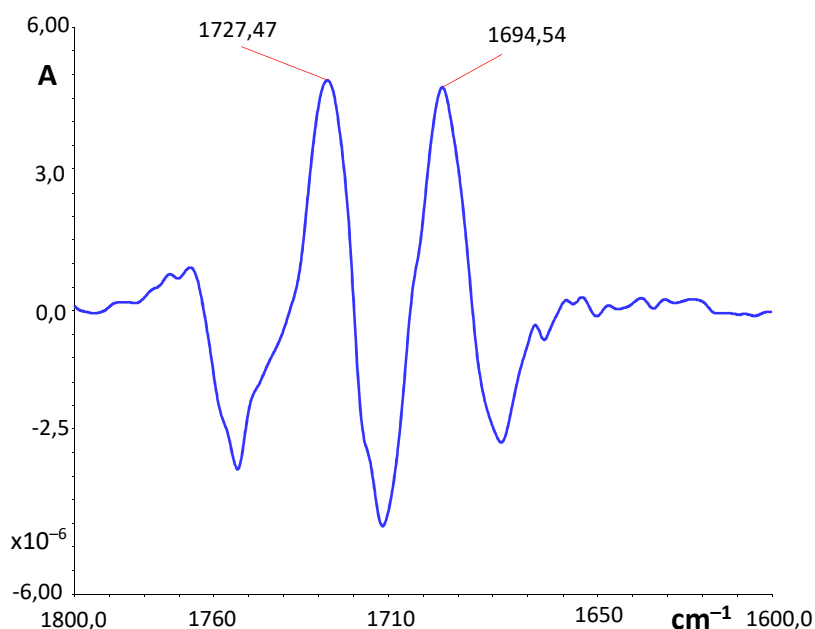


figure 12 shows the fourth derivative of the C=O band at 1702,59 of the spectrum of *figure 11*. This band is composed of two bands.

The band at 1727,47 is the C=O stretching (ester, 1729) of the not reacted Plexiglas. The band at 1694,54 is the C=O stretching of the carboxylic acid COOH (1725-1700). These bands have a lower wave-number compared to the tabulated values. It is necessary to consider that the original Plexiglas is not a pure substance. Moreover, the spectra of *figures 10 and 11* belong to a solid obtained after two reac-

tions and their respective rinsing. It is reasonable to hypothesize that there are some impurities which interfere during the spectra recording.

Introductory remarks

The derivative spectra are calculated according to absorbance as function of the wave-number ($\bar{\nu}$). The derivative spectroscopy refers to a method to process spectra. By this method the slope of the original spectral line is measured; in other words, a measurement of the speed of the absorbance change is taken as a function of the wave-number ($\bar{\nu}$). The spectrum derivative is calculated by the spectrophotometer software using the method of the *numerical differentiation*. By this method a certain number of close points is taken on the spectral line, but they must be split by a wave-number $\Delta\bar{\nu}$. Then the corresponding absorbance difference ΔA is calculated. The ratio $\Delta A/\Delta\bar{\nu}$ is the first derivative of the original spectrum. The same procedure is used to calculate the higher order derivatives. The interval $\Delta\bar{\nu}$ is measured by the number of points: when this number is low, many details are obtained from the derivative spectrum and vice-versa. The value of 37 points (intermediate value among the possible) is chosen because enough details from the spectrum are obtained. The fourth derivative is chosen for two important reasons:

1. the maximum values of the bands of the original spectrum are kept also in the derivative spectrum
2. as the resolution power of the instrument is limited, this can be increased by derivative spectrum. The hidden peaks of the original spectrum, therefore can come out.

HARDNESS OF THE MINERAL WATER BEFORE AND AFTER PERCOLATION THROUGH MICRO-COLUMNS

Properties of the mineral water used as sample ($V=0,5$ L). Table 4 shows the list of the substances as ions, solubilized in 1 L of water.

Table 4

| | | | | | |
|-------------|-------|-----------|------|-----------|-------|
| bicarbonate | 326,0 | magnesium | 18,5 | nitrate | 3,0 |
| calcium | 85,8 | chloride | 6,8 | potassium | 1,2 |
| sulphate | 23,0 | sodium | 4,1 | fluoride | < 0,2 |

The hardness of water is defined as the *concentration of Ca^{2+} and Mg^{2+} solubilized in water and it is expressed in mg/L of CaCO_3 , or in French degrees (10 mg/L $\text{CaCO}_3 \cong 1$ French degree).*

Hardness^[20] is measured by the titration with EDTA^[21] (Ethylene-Diamine-Tetra-Acetic acid, disodium salt) 0,01 M using the EBT^[22] (Eriochrome Black T; solid indicator), in buffered solution at pH=10. The indicator colour changes from red-violet to blue. EDTA and buffer solutions are purchased ready to use (1mL of the EDTA solution is equivalent to 1 mg of CaCO_3).

Figure 13

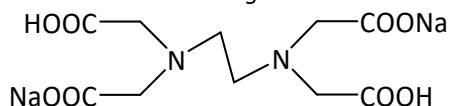
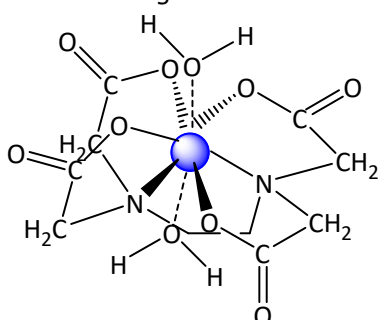
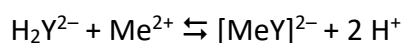


Figure 13 shows the EDTA molecule disodium salt: it can also be written as $\text{Na}_2\text{H}_2\text{Y}$ or $[\text{H}_2\text{Y}]^{2-}$

Figure 14



The reaction between EDTA and Ca^{2+} and Mg^{2+} ions is shown below:



where Me^{2+} is equivalent to Ca^{2+} and Mg^{2+} ions; the combination ratio is 1:1.

The complex molecule between Ca^{2+} ion and EDTA has 8 ligands^[23]. It is shown in figure 14; the Ca^{2+} is the blue sphere in the centre of the complex.

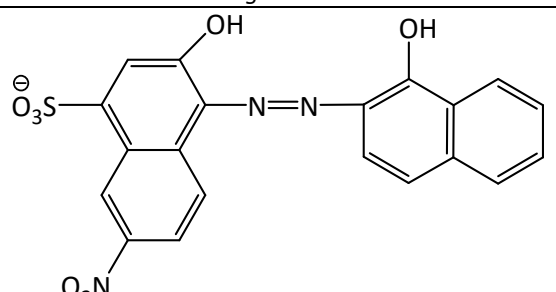
| Figure 15 | | Table 5 | |
|---|--|------------------------------------|--|
|  | | Eriochrome Black T (EBT) indicator | |
| | | Free indicator colour | Colour of the Complex: indicator-metallic ions |
| | | H ₂ In ⁻ red | red-wine |
| | | HIn ²⁻ blue | |
| | | In ³⁻ orange | |

Table 6

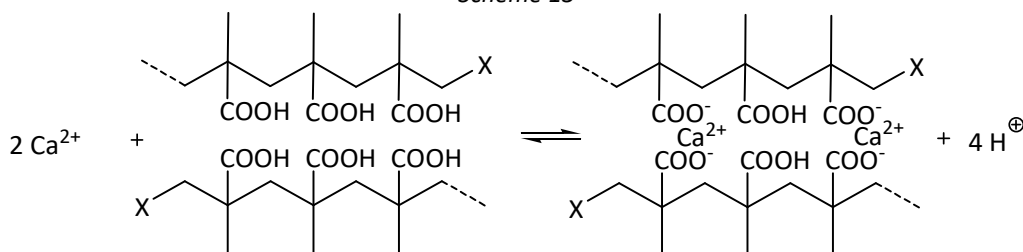
| V(mL) | V(mL) | Hardness |
|------------|-----------|-------------------------|
| water | EDTA | mg CaCO ₃ /L |
| 5 | 0,90 | |
| 5 | 1,05 | |
| 5 | 0,95 | |
| 5 | 1,05 | |
| <V> mL | 0,99 | |
| St.dev.(σ) | 0,075 | |
| <V>±σ (mL) | 0,99±0,08 | 197,5 |
| | | |

The hardness of the mineral water is about 198 mg/L (19,8 French degrees) and it is measured by the EDTA titration. In this titration the colour of the EBT indicator changes from red-wine to blue at the colour change point. The volume of mineral water used is smaller (5mL) than the volume which should be used (between 10 and 25 mL) therefore the result can be wrong. The hardness value is not important for the experiment in progress because only the possible decrease is useful. To perform tests, a volume of 5 mL is chosen because the percolation through the micro-columns allows to collect few mL of water. Moreover, it is necessary to

make sure that columns do not become exhausted because of the reaction of the *scheme 13*.

This shows that Ca²⁺ ions bind to carboxylate ions (COO⁻) of the resin and an equivalent number of protons will be freed in solution, therefore the pH will decrease.

Scheme 13



A volume of ≈12 mL of percolated water through the first column is recovered (percolation speed ≈1 drop per minute). Two small amounts of water (5mL); some mL of the buffer solution and some milligrams of the solid indicator (EBT) are put into two different beakers (50 mL) to measure hardness. The solution colour is immediately blue and not red therefore the EDTA titrant is not needed: it means that the Ca²⁺ and Mg²⁺ ions are completely absent. It means that the cationic exchanging resin obtained from Plexiglas, really works. A second column with a larger opening is prepared with the same method. This column is used to percolate mineral water with a percolation speed of ≈2 drops per minute. The volume of ≈17 mL is recovered. A volume of 5 mL of percolated water is mingled to some mL of the buffer solution and some milligrams of the solid indicator (EBT) to measure hardness. The solution colour is immediately blue and not red therefore the EDTA titrant is not needed: it means that the Ca²⁺ and Mg²⁺ ions are completely absent because they are caught by the exchanging resin. Both the original water and the percolated water are used to measure the pH by means of a pH-meter, previously calibrated.

The pH of the original water is 8; on the contrary the pH of the percolated water through the column is 6,3. After percolation, water gets slightly acid because of the protons release as it is expected by the reaction of the *scheme 13*. The pH decreasing is remarkable (−21%).

SPECTROMETRIC MEASUREMENTS IN THE VISIBLE AND UV RANGES^[24]

Three solutions are prepared: the first contains 5 mL of de-ionized water; the second contains 5 mL of the mineral water which is used in this experiment; the third contains 5 mL of mineral water which is percolated through a third micro-column. A volume of 4 mL of the buffer solution (pH=10) and 0,0025g of the EBT indicator are added to each of these solutions. A "blanc" is also prepared containing 5 mL of de-ionized water and 4 mL of the buffer solution. Spectra of the three solutions are recorded in the visible range from 800 to 400 nm, versus the "blanc". The scansion speed is 240 nm/minute.

Table 7

| <i>Solution + buffer solution + EBT</i> | <i>Solution colour</i> |
|---|------------------------|
| Original mineral water | red-violet |
| Mineral water after percolation through resin | blue |
| De-ionized water | blue |

Figure 16

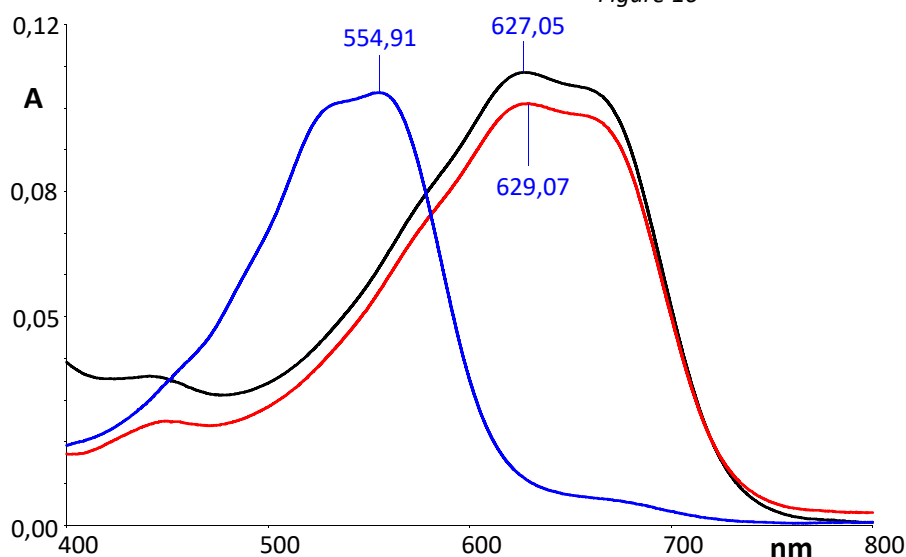


Figure 16 shows the spectra in the visible range, of the solutions prepared as the table 7 highlights.

1. Blue curve: original mineral water
2. Red curve: de-ionized water
3. Black curve: mineral water after percolation through the resin which is obtained from Plexiglas.

The spectral curve of the solution which is obtained from the mineral water percolated through the resin is superimposable to the spectral curve of the de-ionized water. Since de-ionized water does not contain metallic ions then also in the percolate water they are absent.

Figure 17

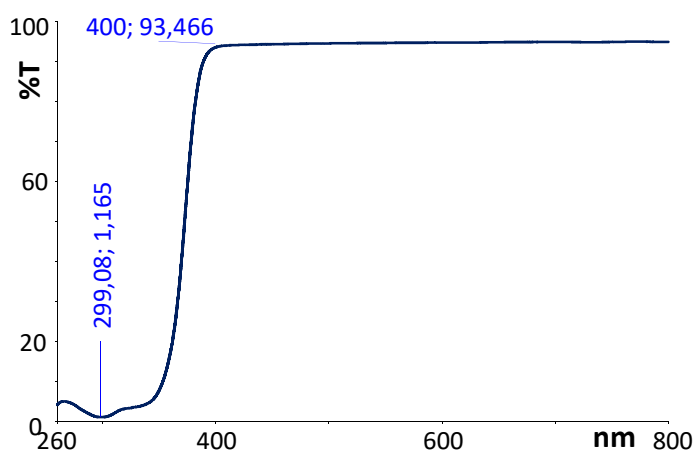


Figure 17 shows the average spectrum of three spectra which are recorded in T%, of the Plexiglas slab (thickness=3mm). The spectrum in the visible range (800-400) is an almost horizontal line and its T% is higher than 93% (in the technical report it is 92%). The T% average should be calculated between 800 and 400 nm but as the spectrum is an almost horizontal line, the value which has been taken is a good approximation. T% quickly decreases in the UV region (wave-length below 400 nm).

CONCLUSIONS

Experimental facts:

1. The IR spectra emphasize the changing of the R-COOCH_3 of the Plexiglas into R-COO^- of the solid after hydrolysis and then the changing into R-COOH group after the acid (HCl) treatment of the hydrolysed solid.
2. The visible spectra of the aqueous solutions prepared as in *table 7*.
3. pH of the mineral water measured before and after the percolation through resin.
4. The capability of this resin to eliminate positive metallic ions such as Ca^{2+} and Mg^{2+} from the water demonstrates that Plexiglas has been really changed into a cationic exchanging resin which has R-COOH groups. The question concerns obtaining a more complete transformation. For this purpose, the following devices would be suitable:
 - i. shaping the original Plexiglas as a "fine dust"
 - ii. using methanol as a solvent because it is a molecule smaller than ethanol and, therefore, can penetrate better inside the micro-granules of Plexiglas. So NaOH is carried better. In this research methanol is not used as it is toxic.
 - iii. performing the reaction at reflux temperature for a suitable time.

This type of resin could be used to "soften" (to reduce hardness) water by the contrivance to correct its pH to about neutrality, after percolation through resin. The possible straw-yellow colour of the softened water can be removed percolating water through an active carbon bed.

In this research investigations about the development of gaseous substances during the alkaline hydrolysis at the reflux temperature have not been carried out.

Notes

- I. The chemical formulas are written by the Chem-Office Pro 8.0 program.
- II. Spectra are recorded by means of IR and Visible-UV spectrophotometers mentioned in the list of instruments.
- III. Photos are taken by students and authorized by the School Principal
- IV. The *table 6* is created by the "excel worksheet" program.

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Plexiglass, mainly polymethylmethacrylate (PMMA) is transparent polymer but very hard to recycle. In this research, the students come up with an idea to hydrolyze the ester side chain to form poly acrylic acid. The negative charge was then utilized to bind cations to apply as cation resins. The idea is very interesting and original. The recycle concepts fit with the environmental issues we are facing today. Although the reaction time is slightly long, the authors also consider safety issue and aim for real application.